# Accurate determinations of Ge atom fractions in SiGe semiconductor chips using high performance ICP-OES

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The Ge atom fractions in SiGe chips with nominal values in the range 3.5% to 14% were accurately determined using high performance inductively coupled plasma optical emission spectroscopy (HP-ICP-OES). For each chip, Si and Ge were determined in separate HP-ICP-OES experiments, and the Ge atom fraction was calculated from the data. This approach eliminated the need to measure the mass of the chip, thereby avoiding a potentially significant source of uncertainty. Digestion of the chips occurred in the presence of HF–HNO<sub>3</sub> at room temperature in closed vessels to prevent the loss of Si as volatile SiF<sub>4</sub>. Recoveries of both Si and Ge in these digests were observed to be effectively 100%. For the Si determinations, NaOH was introduced to reduce Si background and memory. Expanded uncertainties (95% confidence) associated with the Ge atom fractions determined, accounting for all significant components of uncertainty, were observed to be  $\sim 0.2\%$ .

# Introduction

Silicon germanium (SiGe) technology has played a significant role in the development and success of the wireless and computer industries.<sup>1-11</sup> This technology is advantageous as the fabrication process is very similar to that of silicon-based chips.<sup>3,9</sup> The SiGe chips enable a reduction in component size and noise as well as the use of higher frequencies while maintaining the same low power requirements as Si chips. These favorable qualities make SiGe chips competitive with the more expensive III–V semiconductors, such as gallium arsenide (GaAs) and indium phosphide (InP).<sup>14,5</sup> As the popularity of SiGe technology continues to advance in today's electronics market, characterization of these semiconductor chips becomes more vital. Therefore, an increasing need is observed for more accurate and precise analytical measurements and well-characterized reference materials.

In this paper, we describe the use of inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine the stoichiometries of SiGe semiconductor samples. The National Institute of Standards and Technology (NIST) has recently undertaken a project in conjunction with the semiconductor industry to provide chemically characterized SiGe chips to be used for secondary ion mass spectrometry (SIMS) analysis. The characterization project requires accurate and precise determinations of the Ge atom fractions. These ICP-OES measurements are part of this effort.

Kucharkowski *et al.*<sup>12,13</sup> utilized ICP-OES to achieve similar measurements with superconducting materials. Multiple lines (typically 3) were selected for the analyte and internal standard elements in the determination of the stoichiometry. Weighting factors were generated for each line, dependent on calibration sensitivity and measurement statistics. Calibration standards were matrix-matched and covered a range of analyte

Analytical Chemistry Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8391, USA. E-mail: savelas. rabb@nist.gov concentrations (*e.g.*, the highest standard could be a factor of 2-8 larger than the lowest standard). All samples were measured multiple times to improve signal averaging. One calibration standard, matched closely to the analyte concentrations of the samples, was repeatedly measured (external standardization) throughout the experiment to account for drift or disturbances in the sample introduction system. Simultaneous internal standardization was used to correct for short term fluctuations in the experiment. Relative uncertainties in a range from 0.2% to 1.4% are possible using this methodology. The greatest errors were said to result from noise components or biases not appropriately removed during internal or external standardization. It is unclear whether or not the relative uncertainties given in the publications account for all significant components of uncertainty.

Stoichiometric measurements on the SiGe semiconductors in the present study were performed using the high performance ICP-OES (HP-ICP-OES) approach. HP-ICP-OES and the approach used by Kucharkowski et al. 12,13 are similar in principle but differ in execution. The approach of Kucharkowski et al. utilizes volumetric measurements in the preparation of the standards and samples. However, HP-ICP-OES solely uses gravimetric measurements to avoid uncertainties due to temperature and humidity fluctuations. The external standardization of the Kucharkowski approach is limited in its minimization of drift as the repetition of a single standard cannot describe fully the drift behavior observed among all the standards and samples. The time consumed in measuring the same standard before and after every sample for higher accuracy would be better applied to full re-calibrations. HP-ICP-OES utilizes multiple measurements of every standard and sample arranged in a randomized complete block run sequence.<sup>14</sup> In other words, all samples and standards are run once in a randomized sequence, then again in a randomized sequence, and so forth, until the required number of replicate measurements have been obtained. This measurement scheme allows for better measurement statistics in the estimation of the calibration sensitivity as well as a more efficient way of tracking the effect of drift during the experiment.

The drift is effectively removed by fitting a polynomial equation (up to sixth order) to all of the data as a function of time and applying drift correction factors derived from the fitted parameters.<sup>15</sup> Analyte concentrations in the standards and samples are usually closely matched in HP-ICP-OES to prevent uncertainties caused by non-linearity and a non-zero intercept in the calibration. The results of HP-ICP-OES are measurements with small uncertainties, typically of the order of 0.1%, that are directly traceable to the International System of Units (SI).<sup>16,17</sup>

The HP-ICP-OES procedure discussed in this paper is developed and employed for highly accurate determinations of the stoichiometry of SiGe semiconductor material. The method provides a valuable analytical tool for the development of SiGe reference materials as well as for the SiGe industry.

# Experimental

### Instrumentation

A PerkinElmer 3300DV ICP-OES instrument (Shelton, CT, USA)<sup>†</sup> was used for these determinations. The operating conditions can be found in Table 1. These conditions rendered a robust plasma with a Mg II 280.270 nm/Mg I 285.213 nm intensity ratio of 8.4. This value has been corrected for the differing Echelle grating diffraction efficiencies at the two wavelengths by multiplying the observed ratio (4.5) by 1.85.<sup>18</sup> The selection of the internal standard element is typically based on similar chemical behavior to the analyte as illustrated by the periodic table.<sup>14</sup> The selection of the analyte and internal standard wavelengths is based on similar excitation energies as well as favorable intensity ratio precision (0.1% to 0.3% for five replicate measurements). The signals were integrated using a segmented-array charge coupled device detector. Integration parameters were set manually to ensure simultaneous acquisition of the signals.

## Sample preparation

The SiGe samples were small chips having masses ranging from 2 mg to 35 mg with nominal Ge atom fractions of 3.5%, 6.5% and 14%. The chips are described as SiGe 3.5, SiGe 6.5 and SiGe 14, respectively, in this paper. All samples were digested using

Table 1 ICP-OES operating conditions

Plasma gas/L min <sup>-1</sup>	15
Auxiliary gas/L min <sup>-1</sup>	0.5
Nebulizer gas/L min <sup>-1</sup>	0.5
Power/kW	1.5
Viewing	Axial
Sample uptake/mL min <sup>-1</sup>	0.17
Nebulizer	MiraMist
Spray chamber	Cyclone
Analyte wavelengths/nm	Si I 251.611, Ge I 265.118
Reference wavelength/nm	Sn II 189.927
On-chip integration time/ms	256
Total read time/s	8.196

† In order to describe experimental procedures adequately, it is necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular products or equipment are necessarily the best available for that purpose. a HNO3-HF mixture. The digestions of most materials containing Si involve HF, which can result in the loss of Si via the formation of volatile SiF4.19-21 Ge is less prone to loss unless in the presence of HCl.<sup>22-24</sup> A mild digestion technique, similar to that utilized in the digestion of SRM® 295x Silica-On-Filter,<sup>20</sup> was implemented to mitigate the loss of Si. Results obtained during the development of SRM 295x showed complete Si recovery (100.6%  $\pm$  1.4%, expressed as a 95% confidence interval) when gradually increasing the acid concentration of the digest in the absence of an external heat source. The initial digestion of the SiGe chips consisted in adding 2 ml of H<sub>2</sub>O, 1 ml of concentrated HF and 1 ml of concentrated HNO<sub>3</sub> (in that order) to the chips in a 30 ml polyethylene bottle. The bottle was capped and mildly agitated at ambient temperature until the next day. Variations in the digestion procedure were needed in the following days for chips of different Ge atom fractions. The SiGe 3.5 chips were completely dissolved on the second day and diluted to a final appropriate mass. The SiGe 6.5 chips were still visible in solution (no change in appearance) on the second day and an additional 1 ml of concentrated HNO<sub>3</sub> was added. The bottle containing the digest was recapped and mildly agitated. Small pieces of the chip (metallic or white in color) remained on the third day. An additional 1 ml of concentrated HNO<sub>3</sub> was added to the digest and the bottle was recapped and further mildly agitated for  $\sim$ 7 d. Samples were completely dissolved and were diluted to a final mass ( $\sim 20$  g). The SiGe 14 chips remained unchanged like the SiGe 6.5 chips on the second day and an additional 1 ml of concentrated HNO<sub>3</sub> was added to the digest. Upon the addition of acid, bubbles began to evolve from the alloy. Samples were completely digested within 1 h to 2 h and were diluted afterwards.

#### Analytical procedure

HP-ICP-OES employs a careful experimental comparison of a sample with a calibration standard that is prepared to mimic the expected nature of the sample, both in terms of matrix and the analyte mass fraction.<sup>14,16,17</sup> Any observed difference between the sample and standard is used to compute the analyte mass fraction in the sample. An internal standard is used to correct for high-frequency noise, and a drift correction procedure<sup>15</sup> is incorporated to correct for low-frequency noise (*i.e.*, drift). In many cases, HP-ICP-OES can provide elemental determinations with expanded uncertainties, corresponding to 95% confidence intervals, of better than a few parts per thousand.

Four preparations of the calibrants and four preparations of the samples were typically made gravimetrically from SRM<sup>®</sup> 3120a Germanium Standard Solution (Lot No. 000411, 10.00 mg g<sup>-1</sup>  $\pm$  0.03 mg g<sup>-1</sup> Ge), SRM<sup>®</sup> 3150 Silicon Standard Solution (Lot No. 791504, 9.08 mg g<sup>-1</sup>  $\pm$  0.03 mg g<sup>-1</sup> Si), and the SiGe samples. The values given in parentheses for the two SRMs are the certified mass fractions and expanded uncertainties expressed as 95% confidence intervals. The calibrant and sample solutions contained ~20 µg g<sup>-1</sup> Ge and ~4 µg g<sup>-1</sup> Si and were spiked with a 90 µg g<sup>-1</sup> or 400 µg g<sup>-1</sup> Sn internal standard solution to obtain a final Sn mass fraction of ~20 µg g<sup>-1</sup>. The internal standard solution was prepared from a certified reference material (CRM) containing 9985 µg ml<sup>-1</sup> Sn in solution (Inorganic Ventures, Lakewood, NJ, USA).

The two analytes, Ge and Si, were not determined simultaneously using HP-ICP-OES. Rather, two separate analyses were conducted to make the Ge and Si determinations. All determinations, requiring between 1 h and 2 h, consisted of five repeated measurements on the series of dilute solutions in a randomized order, as explained in the Introduction, until each solution had been run five times. For the Ge determinations, it was necessary to match the acid matrix of the calibrants and the samples. After acid digestion, samples were diluted to a final mass using H<sub>2</sub>O while the calibrants were diluted with a HNO<sub>3</sub>-HF mixture that would render a similar acid composition to that of the samples after dilution. For the Si determinations, 0.4 %(m/m) NaOH was used in the dilution of the calibrants and samples. The basicity of the solutions mitigated the Si memory effect. The presence of Na from NaOH far exceeded the Na content of SRM 3150, which is produced from sodium silicate, thereby allowing the calibrants and samples to be matrix-matched. Recovery experiments for both Ge and Si were also conducted using high purity Ge and Si metals as unknowns. Approximately 0.1 g of metal was used in each digest.

#### **Results and discussion**

#### Background interferences and memory effects

Success in accurately determining the Ge atom fractions in the SiGe chips can be challenged by background and memory.



Fig. 1 Analysis of Si and Ge recoveries for the pure metals after acid digestion. The error bars are 95% confidence intervals taking into account all known sources of uncertainty.



**Fig. 2** Experimental drift in the normalized signal of Si I 251 nm as a function of time for all standards and samples. The error bar (95% CI) represents the largest uncertainty observed among the data points.

Extensive Si background and memory can be observed as free fluoride releases Si from components (*e.g.*, spray chamber, injector, torch) of the sample introduction system of the ICP instrument.<sup>25,26</sup> Blank intensities for Si I 251 nm were observed to be  $\sim 3000$  counts s<sup>-1</sup> prior to sample analysis. These intensities dramatically increased to 80 000 counts s<sup>-1</sup> after introduction of a sample. This problem was resolved by neutralizing HF with NaOH. Choi *et al.*<sup>25</sup> used an amine reagent to reduce



**Fig. 3** Drift in the normalized signal of Si I 251 nm (a) after internal standardization (IS) with Sn II 189 nm and (b) after IS and drift correction (DC). The error bar (95% CI) in each plot represents the largest uncertainty observed among the data points.

background in the determination of Si in zirconium and steel samples. The blank intensities for Si I 251 nm in our experiment were observed to decrease to between 1000 counts s<sup>-1</sup> and 2000 counts s<sup>-1</sup> in the basic medium. Typically, the choice of an alkali base would have been avoided to prevent the introduction of solutions containing high dissolved salts potentially clogging the nebulizer and/or injector. However, Na from the base was used to compensate for the Na in the calibrants resulting from sodium silicate in SRM® 3150.

#### Recovery of analytes after acid digestion

The recoveries of Si and Ge after acid digestion of multiple pure Si and pure Ge metal pieces are displayed in Fig. 1. The Si metal pieces were dissolved in a HNO3-HF mixture at room temperature in a capped polyethylene bottle as described previously. Si recoveries were observed to be 100.0%  $\pm$  0.2%. The Ge metal pieces were dissolved in a similar fashion; however, heat was added to shorten the digestion period. If loss of Ge was not observed in the presence of heat, it is highly unlikely there would be a loss in the absence of heat. Ge recoveries were observed to be  $100.0\% \pm 0.2\%$ . The uncertainties for both recovery values are 95% confidence intervals, including all known components of uncertainty. No significant loss or gain was observed for either Si or Ge. Therefore, the above protocol could be applied to the semiconductors without heat to minimize loss of Si. Si and Ge measurements were not performed simultaneously because

of errors (95% confidence) in the range of 0.2-0.3% in the Ge analysis as a result of the basic medium. Therefore, Ge measurements were performed in acid with matrix-matched standards.

#### Analysis of SiGe chips

HP-ICP-OES was used to analyze the SiGe chips as described earlier. An example of the experimental drift in the Si I 251 nm emission during the analysis of a SiGe 3.5 chip is shown in Fig. 2. The raw Si I 251 nm signal for a given run of a given sample was normalized to the average Si I 251 nm signal for that sample to simplify the comparison among the different samples. The RSD of all normalized signals was 3.2%. This variability was effectively improved by a factor of 11, to 0.28% (Fig. 3a), when Sn II 189 nm was utilized as an internal standard. A cubic polynomial has been fit to the Si/Sn ratio data as a function of time to determine the appropriate correction for the long-term drift. Fig. 3b demonstrates that the drift correction reduces the variability among the sample measurements to 0.11%. Figs. 4 and 5 show the results of the Si and Ge analyses of four aliquot solutions from the same digested SiGe 3.5 chip before and after internal standardization and drift correction. The relative uncertainties in the Si determinations of the four solutions (Fig. 4), expressed as 95% confidence intervals accounting for all sources of uncertainty, decreased from 3.3% to 0.2%after the correction. Similar improvements were observed in Fig. 5 for the Ge determinations in the SiGe chips.



SiGe aliquot solutions

Fig. 4 Comparison of Si results from SiGe 3.5 chip (a) before and (b) after IS and DC. Error bars are expressed as 95% confidence intervals.

Fig. 5 Comparison of Ge results from SiGe 3.5 chip (a) before and (b) after IS and DC. Error bars are expressed as 95% confidence intervals.

Table 2 Si/Ge atom ratio and Ge atom fraction results for all of the SiGe samples using HP-ICP-OES and INAA. The atom ratios were calculated from the Si and Ge values determined experimentally. The atom fractions were then calculated directly from the atom ratios.  $U^{a}$  and U (%) represent the uncertainty and relative uncertainty, respectively

Si/Ge atom ratio	SiGe 3.5			SiGe 6.5			SiGe 14		
		U	U (%)		U	U (%)		U	U (%)
Sample 1	23.13	0.07	0.30	14.04	0.04	0.30	6.00	0.02	0.30
Sample 2	23.72	0.07	0.31	14.33	0.05	0.32	5.94	0.02	0.29
Average	23.42	0.05	0.22	14.19	0.03	0.22	5.97	0.01	0.21
Ge atom fraction (%)		U	U (%)		U	U (%)		U	U (%)
Sample 1	4.14	0.01	0.30	6.65	0.02	0.30	14.28	0.04	0.30
Sample 2	4.05	0.01	0.31	6.52	0.02	0.32	14.40	0.04	0.29
Average	4.10	0.01	0.22	6.58	0.01	0.22	14.34	0.03	0.21
Ge atom fraction (%) INAA	4.17	0.02	0.58	6.56	0.04	0.61	14.34	0.09	0.61
<sup><i>a</i></sup> Uncertainties are 95% confide	nce intervals	accounting f	or all known s	sources of un	certainty.	0101	1 110 1	0107	0101

The Si/Ge atom ratios and Ge atom fractions for all of the Si/Ge atom ratios from the Si and Ge values determined using HP-ICP-OES eliminated the mass of the Si/Ge chips, therefore removing the uncertainty contribution from the balance. Owing to the small masses of the chips ( $\leq$ 35 mg), the balance measurements could have been hindered by electrostatic effects and/or surface oxidation. The Ge atom fractions were subsequently calculated directly from the Si/Ge atom ratios using the following equation:

$$x_{\rm Ge} = \left(\frac{1}{1+r}\right) \times 100\tag{1}$$

where  $x_{Ge}$  is the Ge atom fraction and *r* is the Si/Ge atom ratio. It is assumed that the chips were composed of only Si and Ge. The differences observed among the individual chips of similar Ge atom fraction are likely due to heterogeneity, as shown by electron probe microanalysis (EPMA).<sup>27</sup> The smallest heterogeneity observed was of the order of 1%. The relative uncertainties (95% confidence) for the average ratios and atom fractions were of the order of 0.2% for HP-ICP-OES, accounting for all known sources of uncertainty.<sup>28,29</sup> Comparison with instrumental neutron activation analysis (INAA)<sup>27</sup> in Table 2 shows consistency with HP-ICP-OES results for the SiGe chips. The larger discrepancy in the results for SiGe 3.5 is likely due to material heterogeneity as EPMA results showed heterogeneity decreased in the SiGe chips as the Ge atom fraction increased.

#### Conclusion

In order for SiGe technology to remain competitive in the electronics market, it is essential that characterization of SiGe materials be accurate for the manufacture of reliable products. The Ge atom fractions were successfully determined for three different SiGe chip compositions using HP-ICP-OES. Expanded uncertainties, expressed as 95% confidence intervals and accounting for all known sources of uncertainty, were of the order of 0.2% relative for all three compositions. The experimental design eliminated the need to know the mass of a given chip sample, thereby avoiding a potentially large component of uncertainty. The loss of Si due to the presence of HF was thwarted by digesting the samples at ambient temperature in a closed environment. Si background and memory were greatly minimized with the

introduction of base. The HP-ICP-OES methodology described here may find implementation in the electronics industry. Moreover, the accuracy of the technique allows for its utilization in the future certification of SiGe reference materials.

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